Supporting Information:

Potential-Dependent Hysteresis of Ion Density and Structure of Ionic Liquid at Gold Electrode Interface: In Situ Observation by Surface-Enhanced Infrared Absorption Spectroscopy

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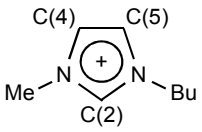
Table t1. Vibrational frequencies (cm^{-1}) and assignments of [BMIM][TFSA].

SEIRAS	IR transmission	Calculation	Assignment	Band intensity
3171	3157	3178[a]	$\nu_s(C(4)HC(5)H)_{ring}$	I_{ring}
3120	3123	3122[a]	$\nu_{as}(C(4)HC(5)H)_{ring}$	I_{ring}
3105	3105	3122[a]	$\nu(C(2)H)_{ring}$	I_{ring}
2959	2969	2957[a]	$\nu_{as}(CH_3)_{alkyl}$	I_{alkyl}
2934	2941	2939[a]	$\nu_{as}(CH_2)_{alkyl}$	I_{alkyl}
2874	2882	2874[a]	$\nu_s(CH_3)_{alkyl}$	I_{alkyl}
2863	2870	2874[a]	$\nu_s(CH_2)_{alkyl}$	I_{alkyl}
1357	1355	1323[b]	$\nu_{as}(SO_2)$	I_{SO}
1327	1332	1300[b]	$\nu_{as}(SO_2)$	I_{SO}
1238	1230	1234[b]	$\nu_s(CF_3)$	I_{CF}
1221	1203	1205[b]	$\nu_{as}(CF_3)$	I_{CF}
1134	1140	1112[b]	$\nu_s(SO_2)$	-
1060	1059	999[b]	$\nu_{as}(SNS)$	-

ν: stretching, s: symmetric; as: asymmetric; and C(2), C(4) and C(5): indicated below.

a: Katsyuba, S. A.; Zvereva, E. E.; Vidis, A.; Dyson, P. J. *J. Phys. Chem. A* **2006**, *111*, 352.

b: Herstedt, M.; Smirnov, M.; Johansson, P.; Chami, M.; Grondin, J.; Servant, L.; Lassègues, J. C. *J. Raman Spectrosc.* **2005**, *36*, 762.



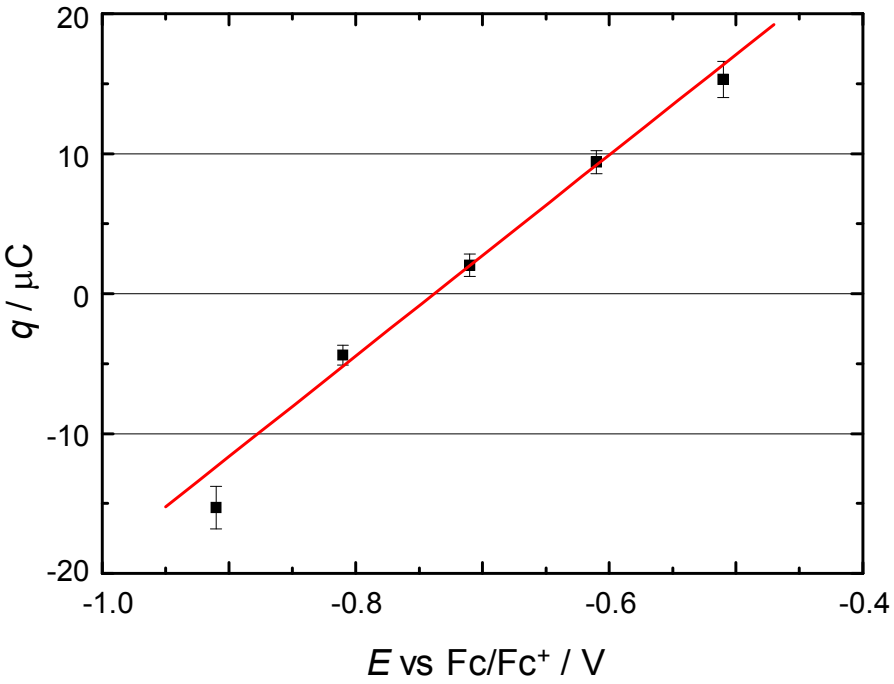


Figure s1. The measured charge as a function of electrode potential for the gold electrode in [BMIM][TFSA] in vacuum condition (5 x 10^{-4} Pa). The charge of the electrode, q, was obtained by integrating the measured current flowing for a minute after dipping. This procedure was performed for 10 times, and the averaged value is plotted for each potential. Red line is an approximated line of $q(E)$ which is obtained by least square fitting. The potential of zero charge is derived as -0.68 V from the intercept of $q = 0$ and $q(E)$. Clean gold wires were used as the working electrode. A platinum mesh was used as a counter electrode. The reference electrode consisted of a silver electrode immersed in [BMIM][TFSA] saturated with $AgCF_3SO_3$, which was separated from the analyte with a Vycor glass filter.

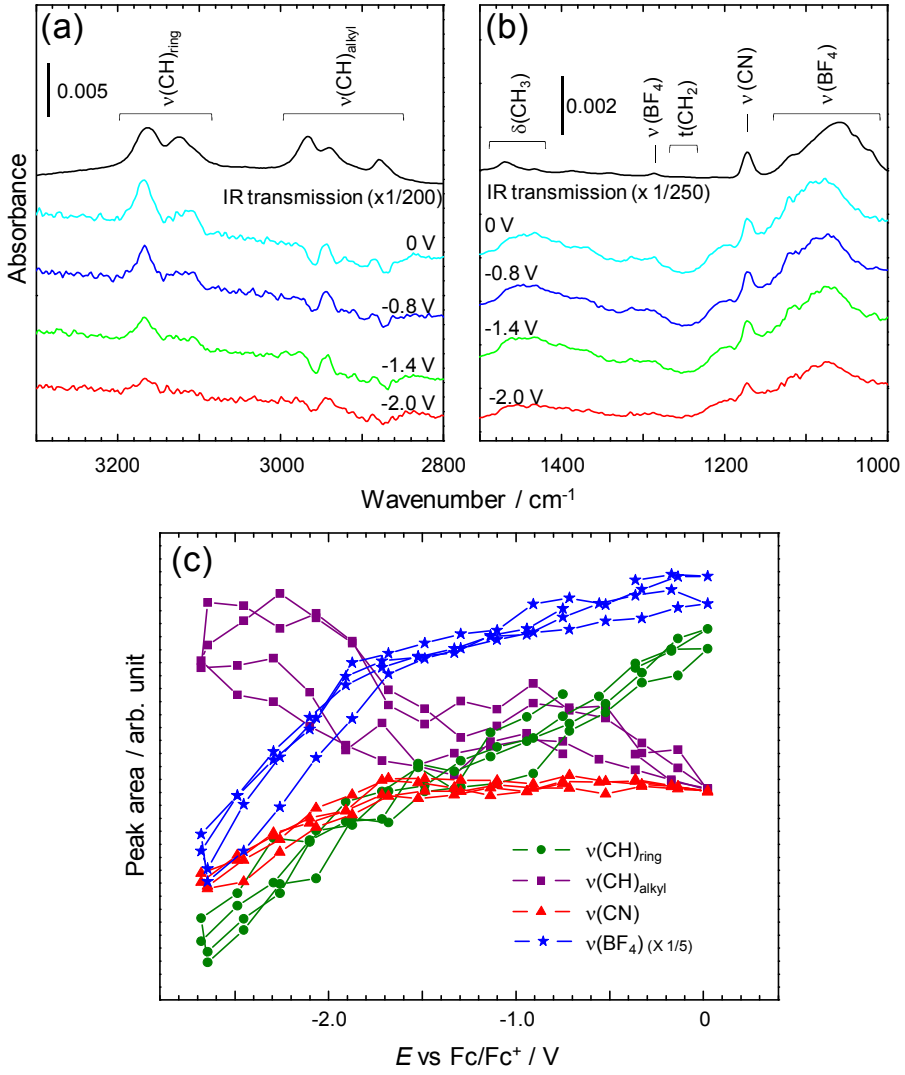


Figure s2. (a) and (b) SEIRA spectra of [BMIM][BF_4]/Au recorded at various electrode potentials during positive potential scan at 40 mV/s. The reference spectrum was collected at -2.6 V vs Fc/Fc^+. All the experimental procedure is identical to that of [BMIM][TFSA]/Au. (c) SEIRAS band intensities as a function of electrode potential. The results of two cycles of potential scans (40 mV/s) which start and end at -0.5 V are shown.